REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*
July 2015

2. REPORT TYPE
Briefing Charts

3. DATES COVERED *(From - To)*
July 2015-July 2015

4. TITLE AND SUBTITLE
FLUORINATED SILSESQUIOXANES: STRUCTURE, SOLUBILITY, AND WETTING (Briefing Charts)

5a. CONTRACT NUMBER
In-House

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
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5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER
Q0BG

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
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8. PERFORMING ORGANIZATION REPORT NO.

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)
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10. SPONSOR/MONITOR'S ACRONYM(S)

11. SPONSOR/MONITOR'S REPORT NUMBER(S)
AFRL-RQ-ED-VG-2015-299

12. DISTRIBUTION / AVAILABILITY STATEMENT
Distribution A: Approved for Public Release; Distribution Unlimited.

13. SUPPLEMENTARY NOTES
Briefing Charts presented at 250th ACS National Meeting; Boston, MA; 16-20 August 2015. PA#15445.

14. ABSTRACT

Briefing Charts

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF: a. REPORT	b. ABSTRACT	c. THIS PAGE	17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
					Joseph Mabry
Unclassified	**Unclassified**	**Unclassified**	SAR	30	**19b. TELEPHONE NO** *(include area code)* 661-275-5857

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std. 239.18

Silicones & Silicone-Modified Materials

ACS Fall National Meeting - Boston

FLUORINATED SILSESQUIOXANES: STRUCTURE, SOLUBILITY, AND WETTING

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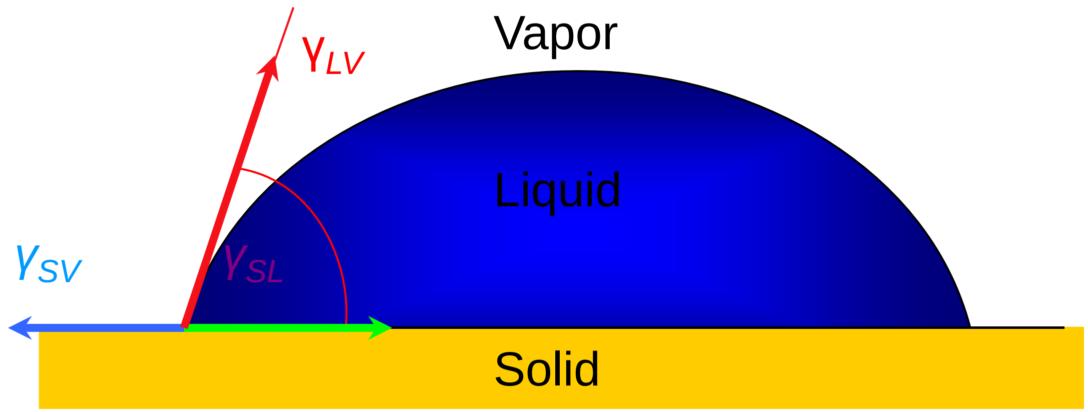
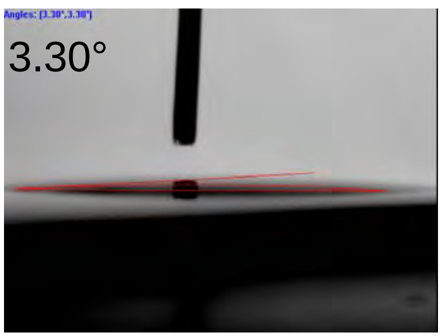
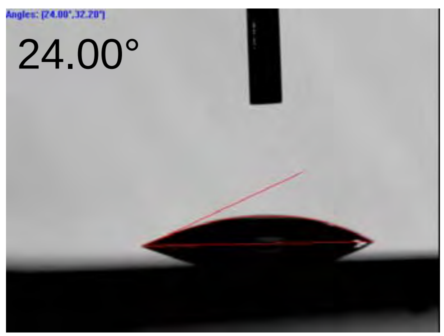
AFOSR

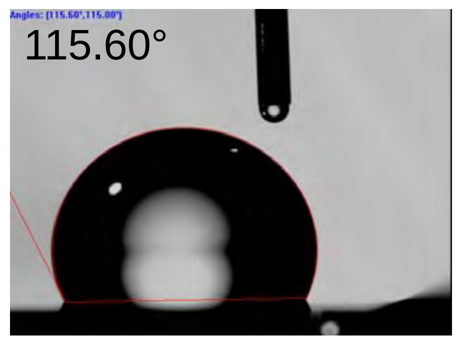
Non-wetting surfaces

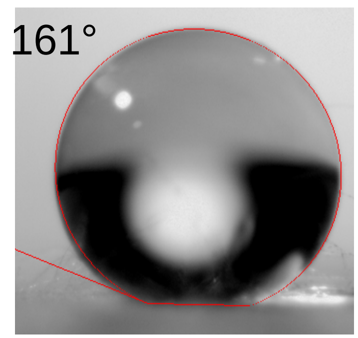


Contact angles with water:









Superhydrophilic
$\theta \sim 0°$

Hydrophilic
$0° < \theta < 90°$

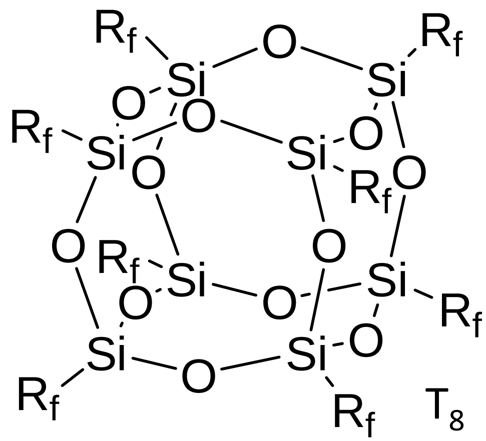
Hydrophobic
$\theta > 90°$

Superhydrophobic
$\theta^* > 150°$

Similarly, superoleophobic surfaces display contact angle $\theta^* > 150°$ with oils or alkanes

Fluorinated POSS Synthesis

$$R_fSiX_3 \xrightarrow[\text{solvent}]{OH^-/H_2O}$$

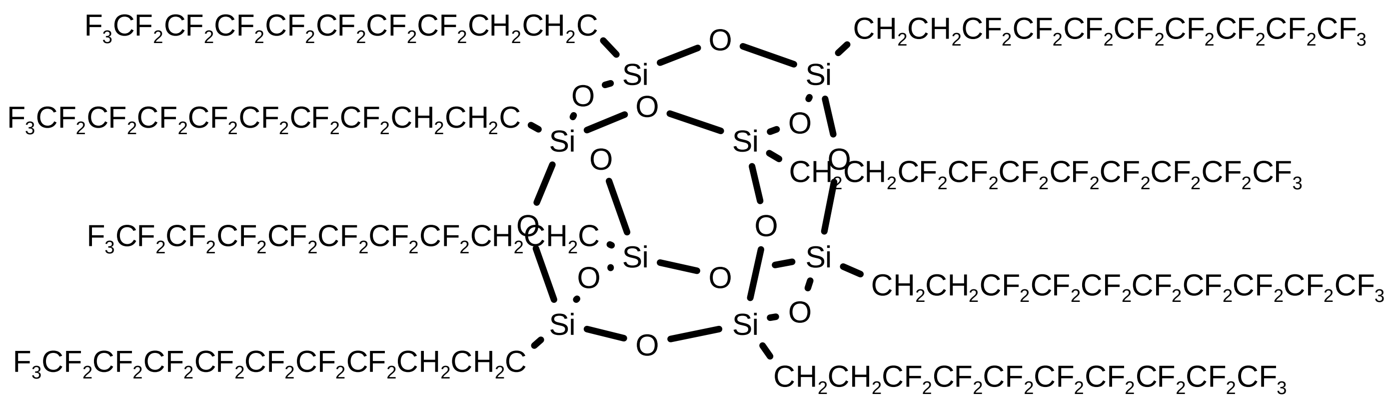


T_8

R_f = $-CH_2CH_2(CF_2)_nCF_3$

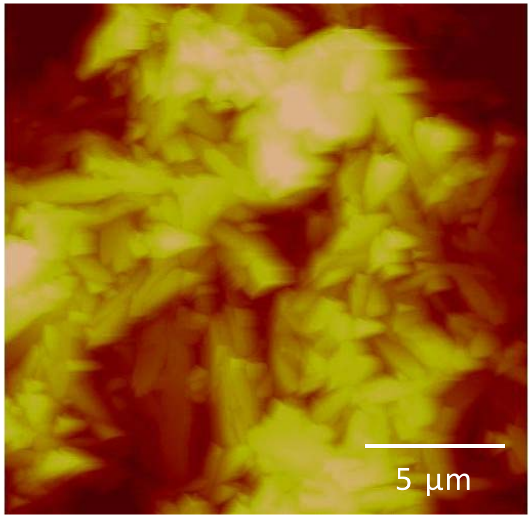
n = 0, 3, 5, 7

- Crystalline solids
- Soluble in fluorinated solvents

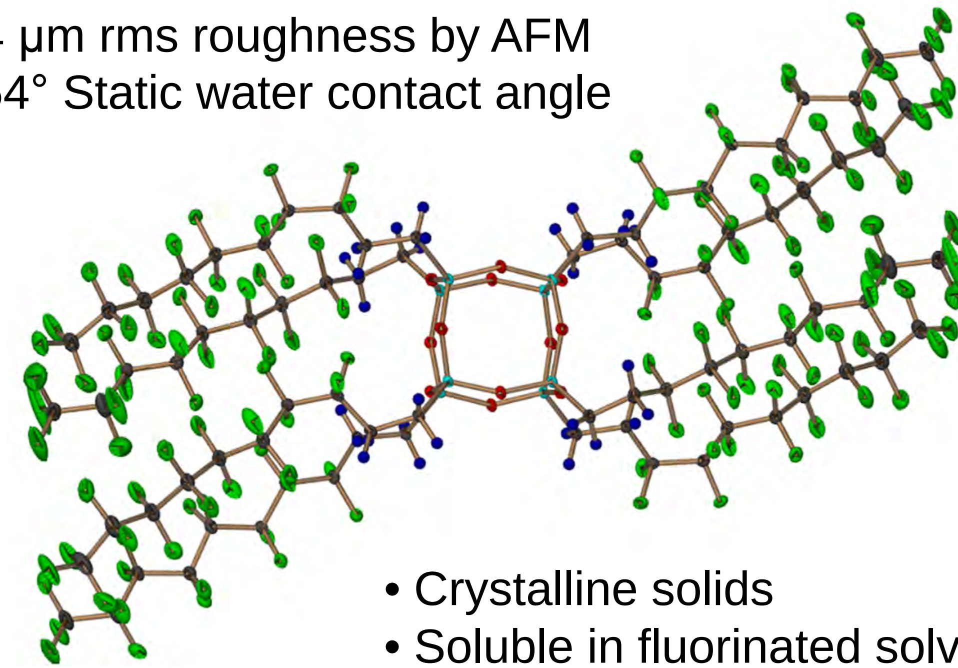


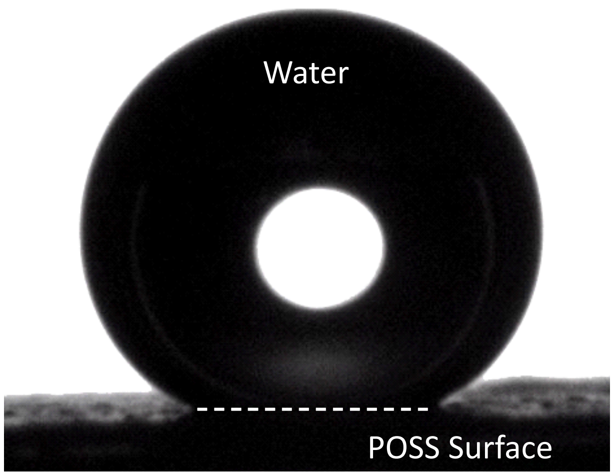
Angew Chem, 2008

Hydrophobic Materials



- Spin-cast surface of FD POSS
- ~4 µm rms roughness by AFM
- 154° Static water contact angle





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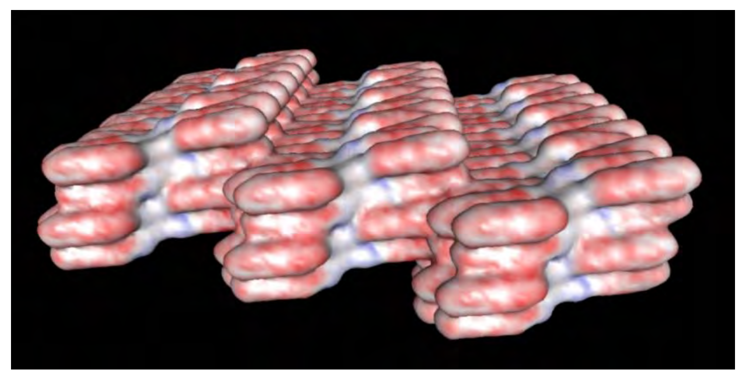
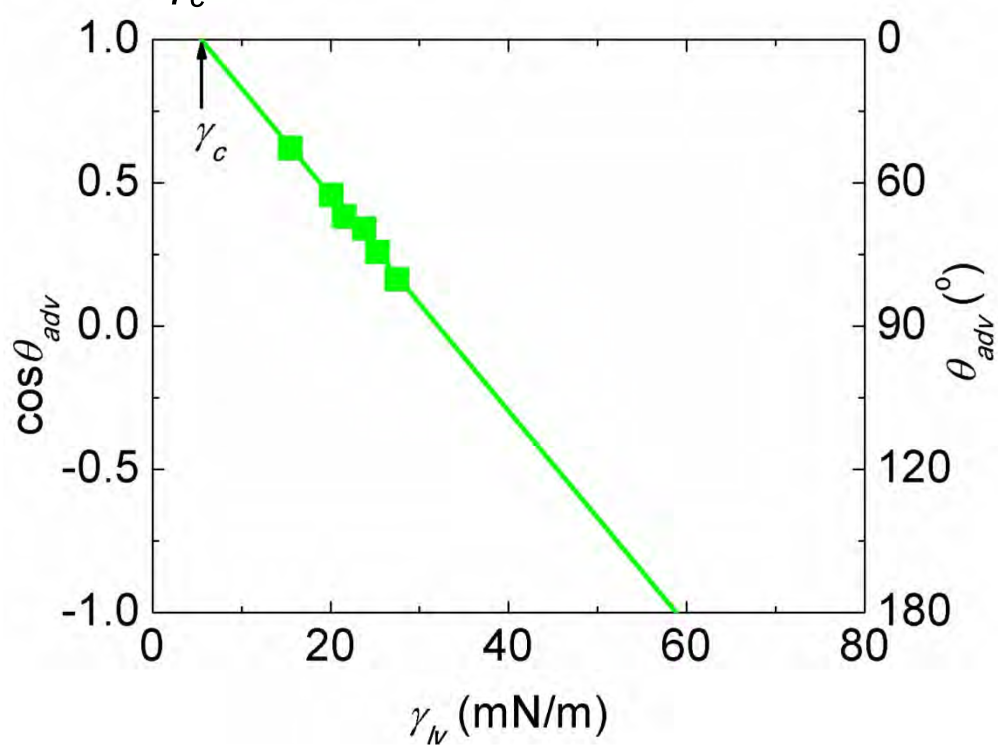
- Soluble in fluorinated solvents

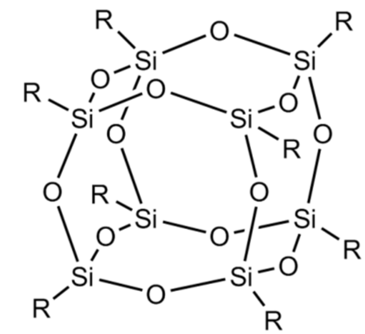


Angew Chem, 2008

Zisman Analysis

γ_c = 5.5 mN/m





Fluorodecyl:
R = $-CH_2-CH_2-(CF_2)_7-CF_3$

GG analysis results in surface energy calculation of: γ_c = 8 mN/m

PTFE ~18 mN/m
PDMS ~24 mN/m

Contacting liquids:
hexadecane (γ_{lv} = 27.5 mN/m), dodecane (25.3), decane (23.8), octane (21.6), heptane (20.1) and pentane (15.5)

ACS AMI, 2010

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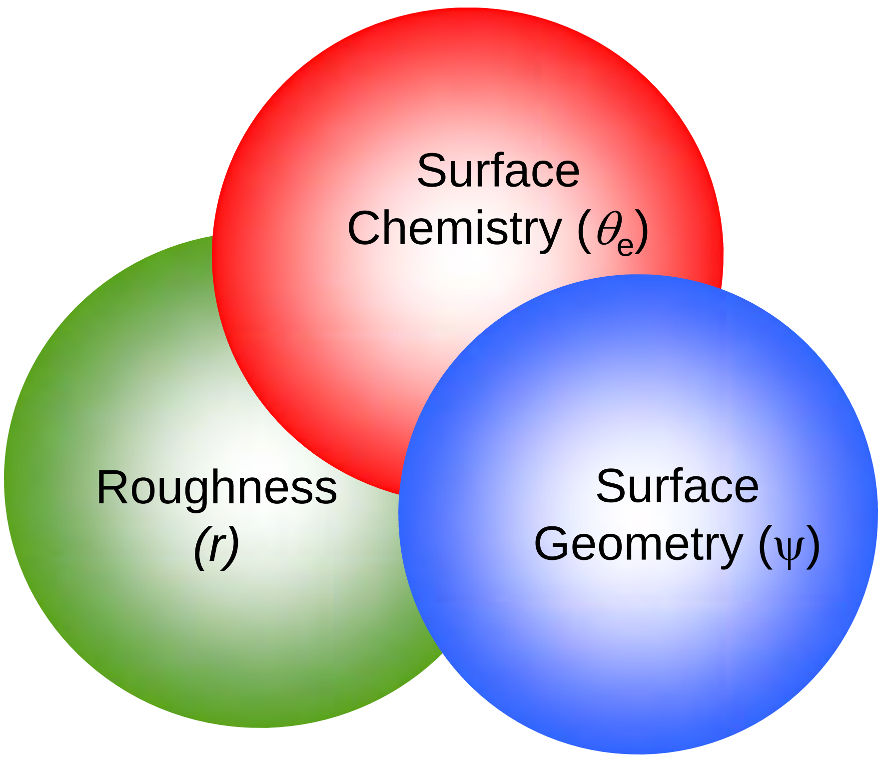
Designing Omniphobic Surfaces

- **Constructing super-repellent surfaces**
  - Three key ingredients



PMMA + 44 wt% POSS
electrospun coating (beads on a string) morphology

Science, 2007

Omniphobic Fabrics Repel "Everything" (even "Wetting" Fluids)

Nylon shell fabric bonded to a Gore–Tex membrane

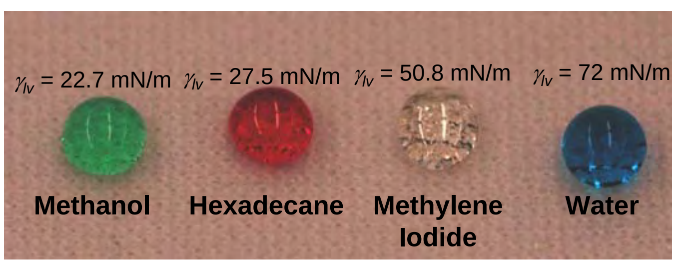
Dodecane

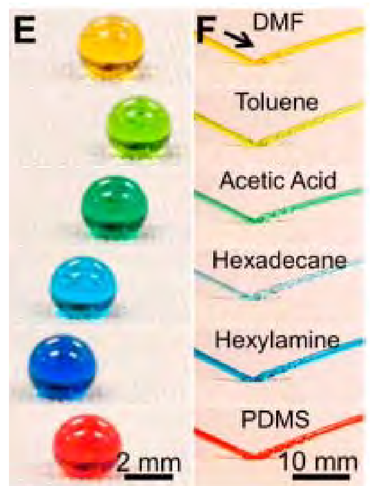
Ethylene glycol

Rapeseed oil

Water

Anticon 100 polyester fabric





JACS, 2013

Adv Mater, Langmuir, 2008

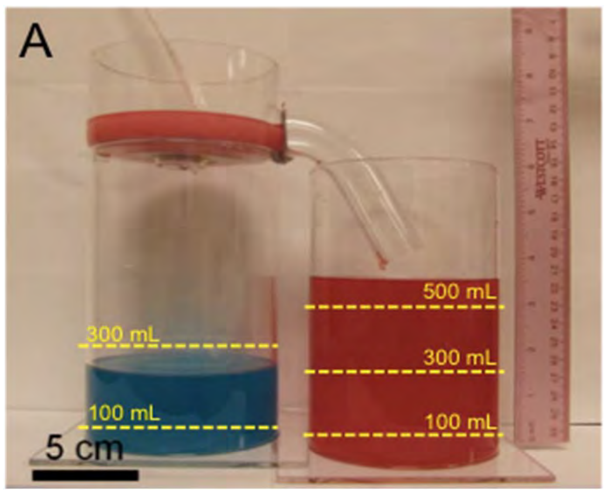
Separation of Oil-Water and Emulsions

- Developed simple membranes and apparatus for gravity-driven, continuous separation of oil-water emulsions.

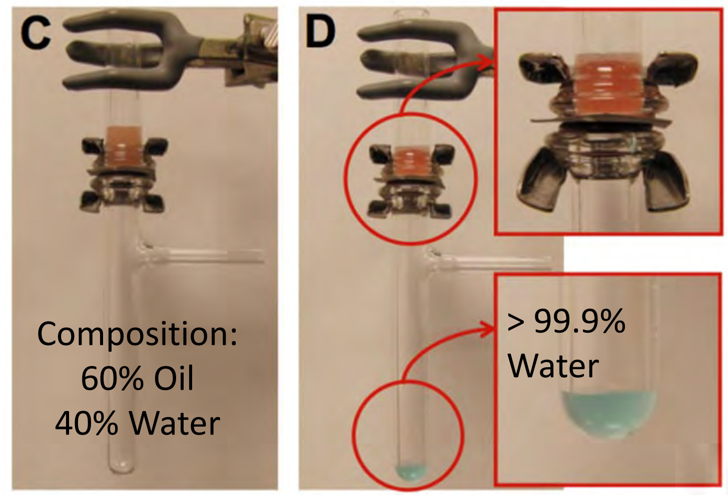
Superhydrophobic/
Superoleophilic

Science, 2007

Gravity Driven - Continuous Flow

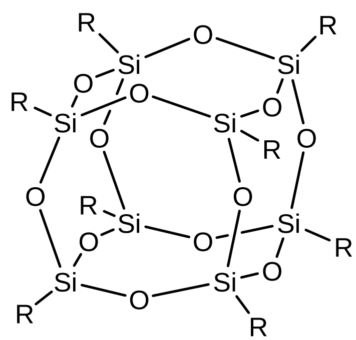


Emulsion Separation

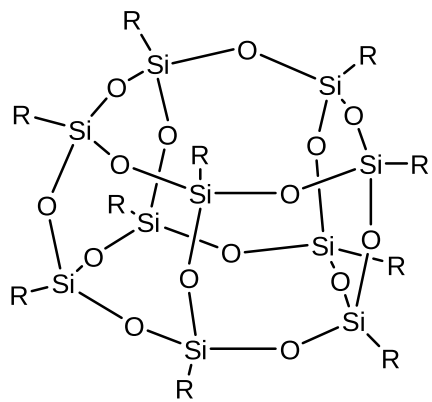


Nature Comms, 2012

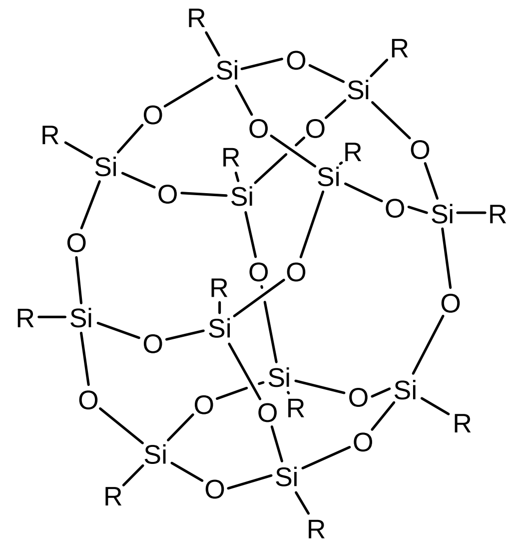
Not all F-POSS are the same!



T_8



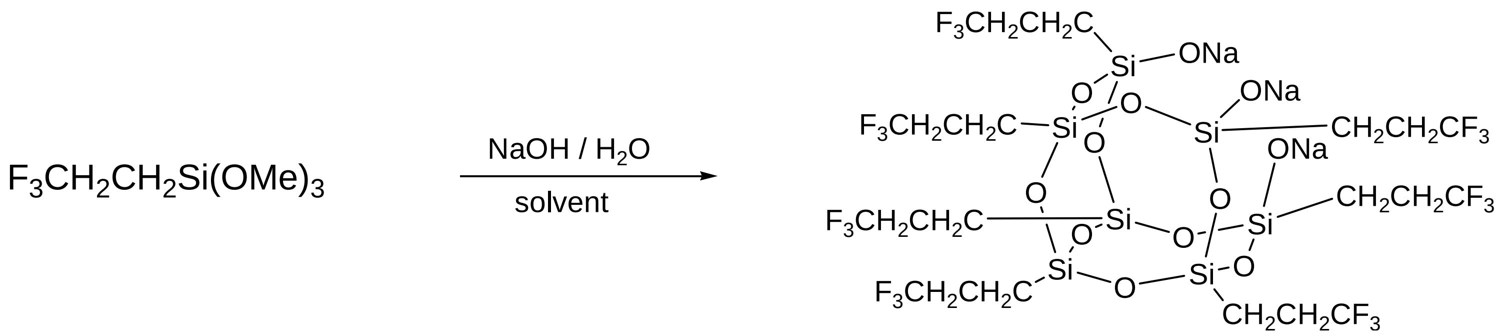
T_{10}



T_{12}

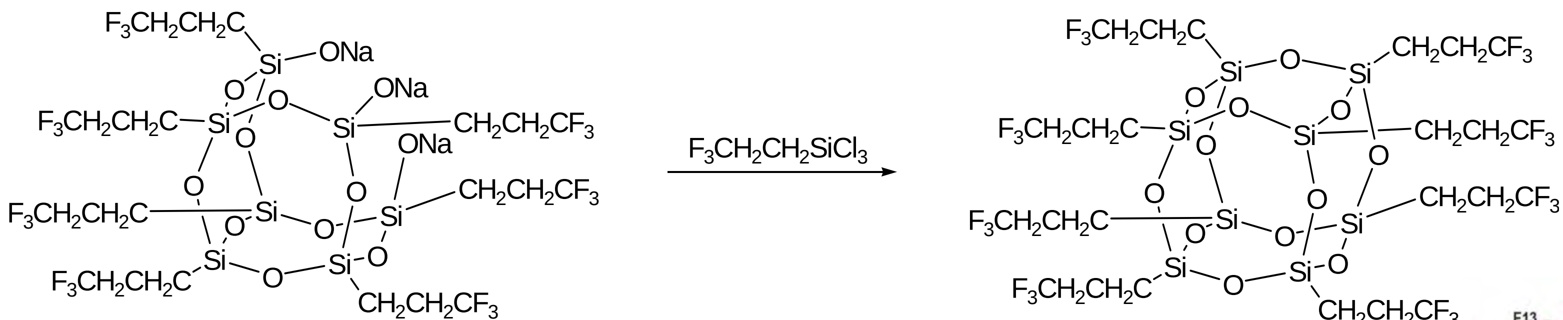
Most common compounds found in a cage mixture

Fluoropropyl$_8$T$_8$

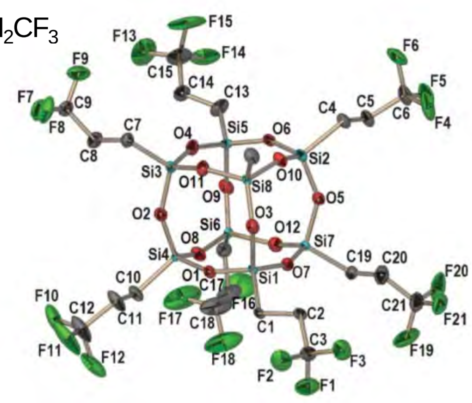


Trisodium salt from trimethoxy silane

Fukuda, *Macromolecules,* 2005



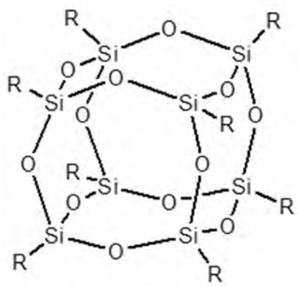
T$_8$ from trisodium salt

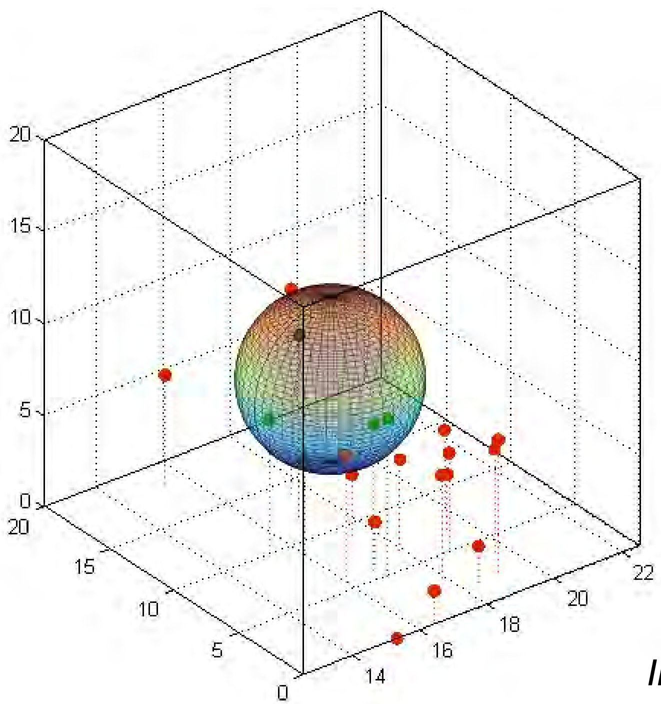


Chem Comm, 2007

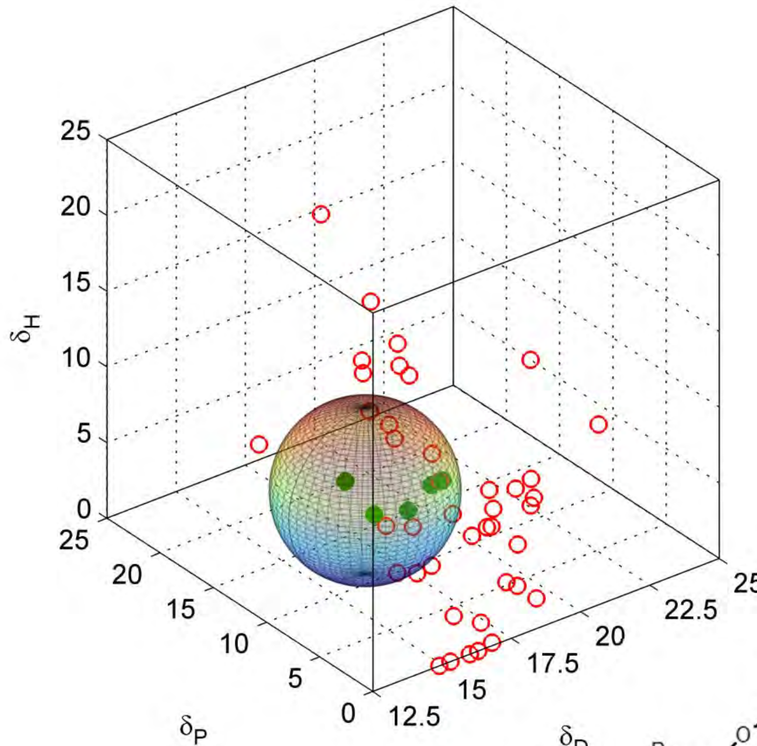
HSP Data for TFP Compounds

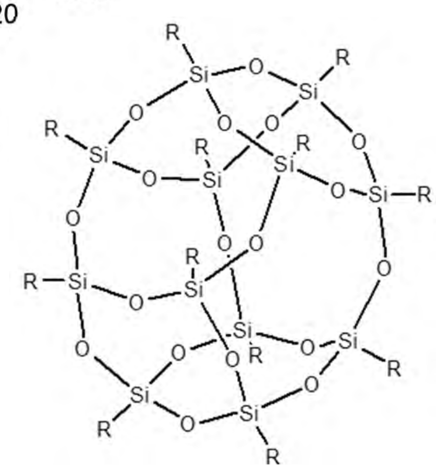
Octa-trifluoropropyl-POSS





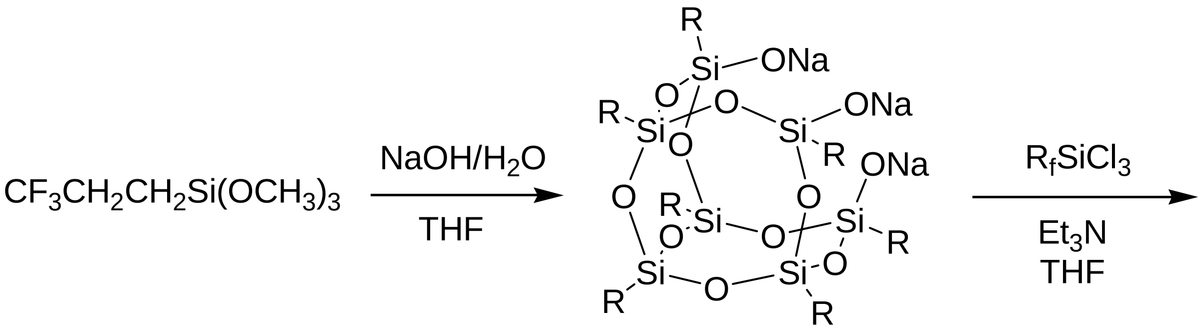
Dodeca-trifluoropropyl-POSS





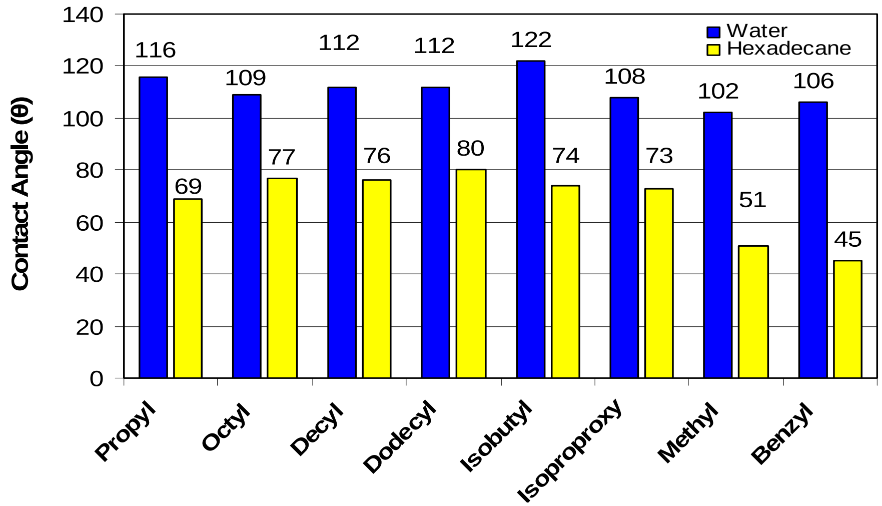
Ind Eng Chem Res, 2012

Corner-Capped F-POSS



R = $CH_2CH_2CF_3$

R_f = $CH_2CH_2CF_3$, $CH_2CH_2(CF_2)_5CF_3$, $CH_2CH_2(CF_2)_7CF_3$, $CH_2CH_2(CF_2)_9CF_3$, $CH_2CH(CF_3)_2$, $CH_2CH_2CH_2OCF(CF_3)_2$

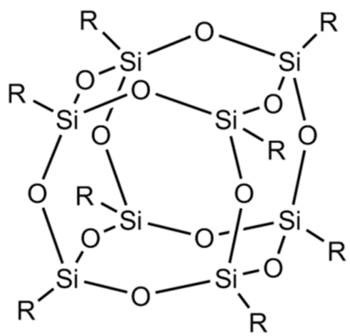


- Diverse architectures – linear, branched, ether
- Corner cap yields moderate to good (73–83 %)
- Soluble in common organic solvents

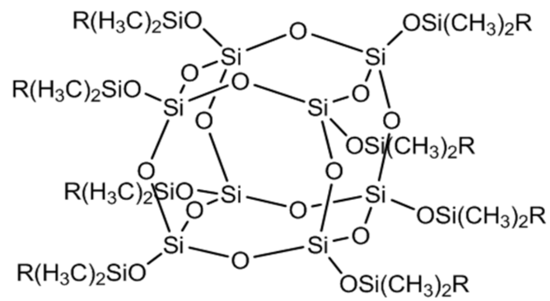
Chem Comm, 2007

Solid Surface Energy Estimation

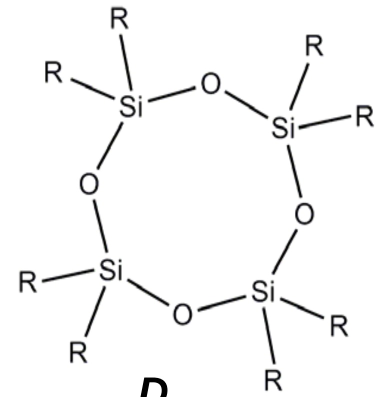
Structure of candidate molecules



T_8



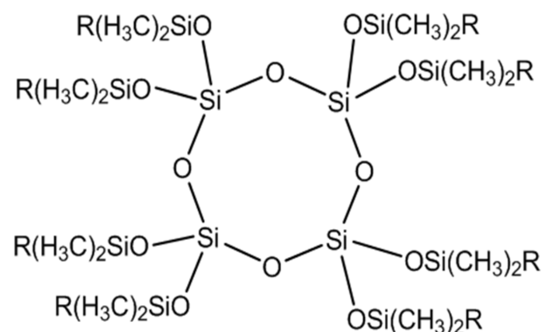
Q_8M_8



D_4

$$F_3C(F_2C)_7(H_2C)_2(H_3C)_2Si{-}O{-}Si(CH_3)_2(CH_2)_2(CF_2)_7CF_3$$

Linear disiloxane resin (***M_2***)



Q_4M_8

Fluorodecyl: $R_f = -CH_2CH_2(CF_2)_7CF_3$

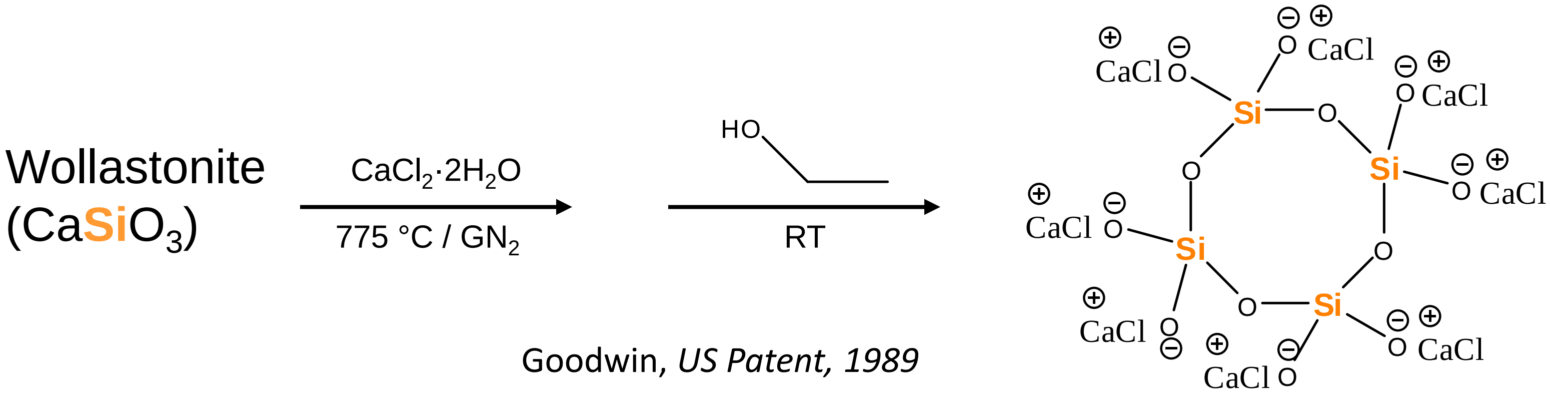
Fluorooctyl: $R_f = -CH_2CH_2(CF_2)_5CF_3$

Fluorohexyl: $R_f = -CH_2CH_2(CF_2)_3CF_3$

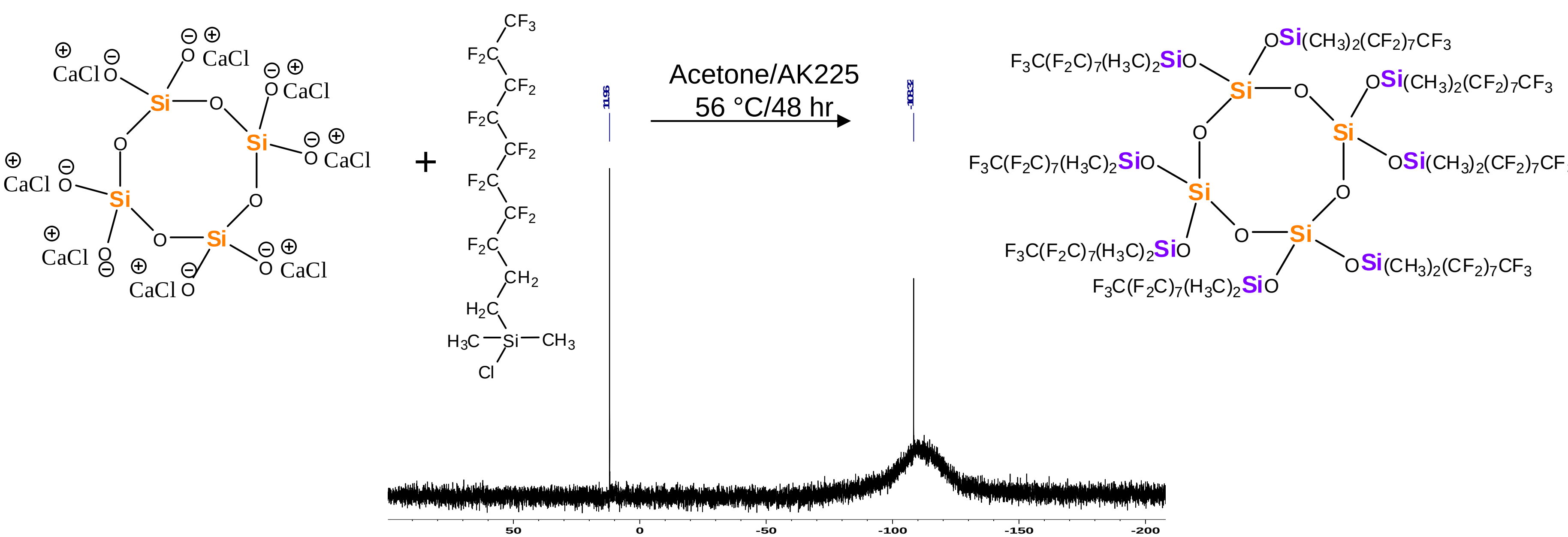
Fluoropropyl: $R_f = -CH_2CH_2CF_3$

ACS AMI, 2010

Q_4 FluoroDecyl Synthesis



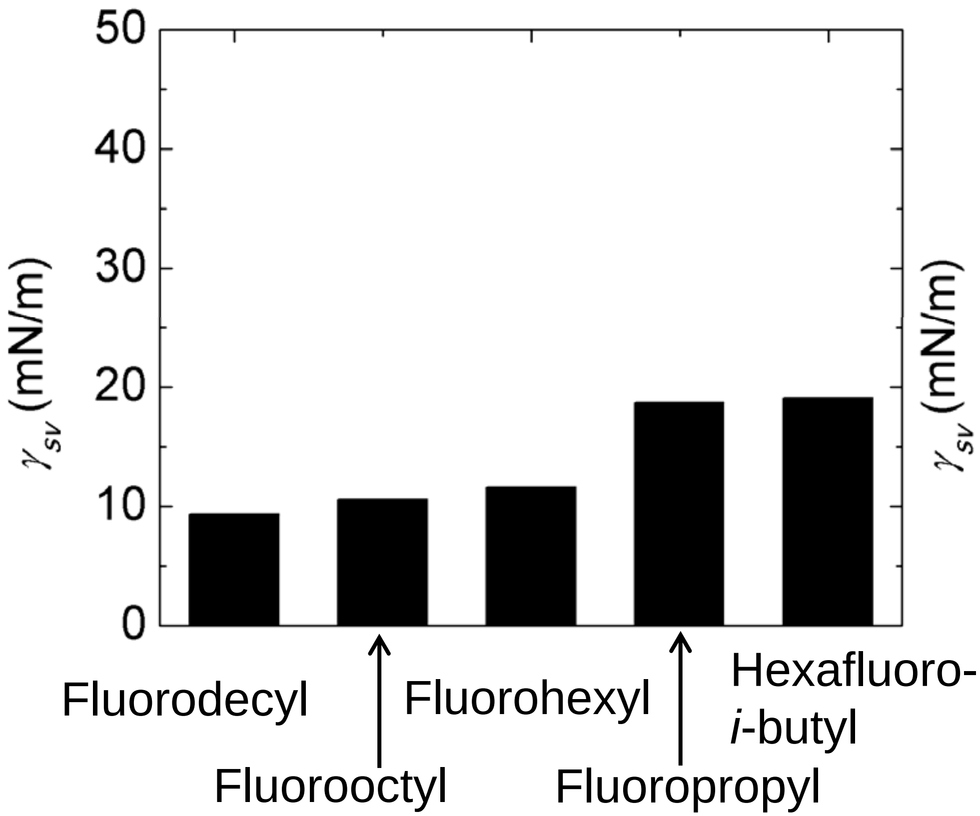
Goodwin, *US Patent, 1989*

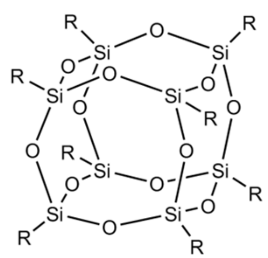


ACS AMI, 2010

Solid Surface Energy (γ_{sv}) via Girifalco-Good Method

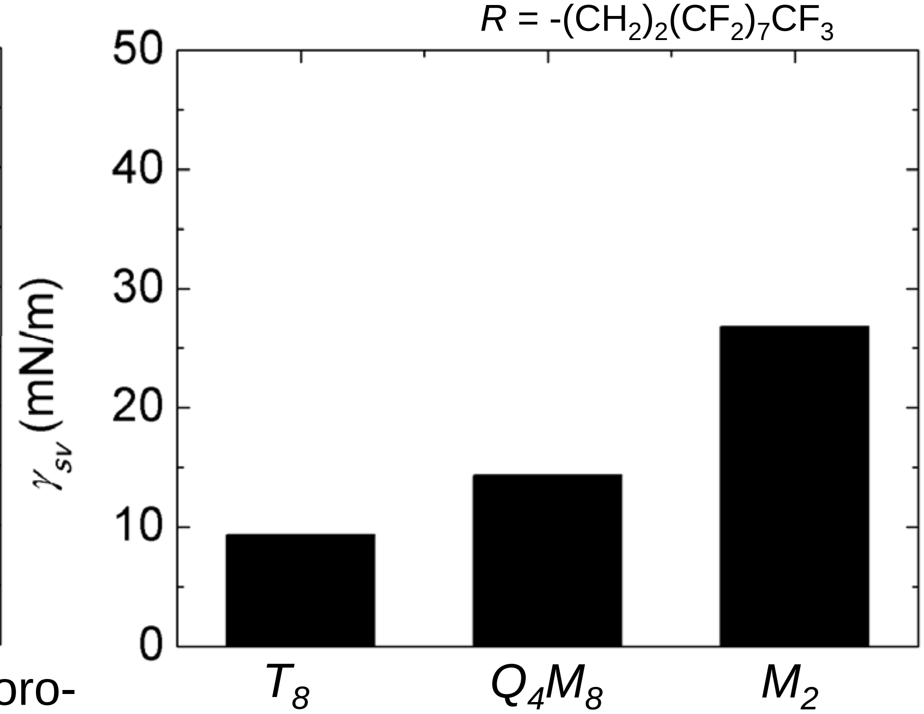
Molecules with a T_8 cage

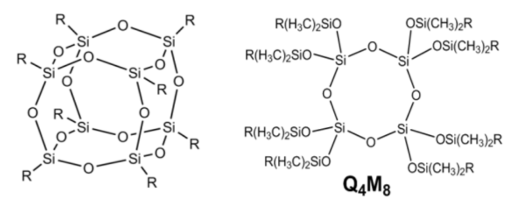




Molecules with a fluorodecyl chain

R = -$(CH_2)_2(CF_2)_7CF_3$





$F_3C(F_2C)_7(H_2C)_2(H_3C)_2Si-O-Si(CH_3)_2(CH_2)_2(CF_2)_7CF_3$

ACS AMI, 2010

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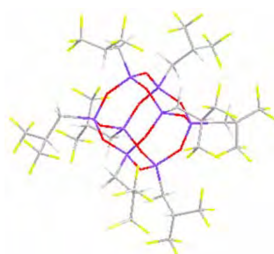
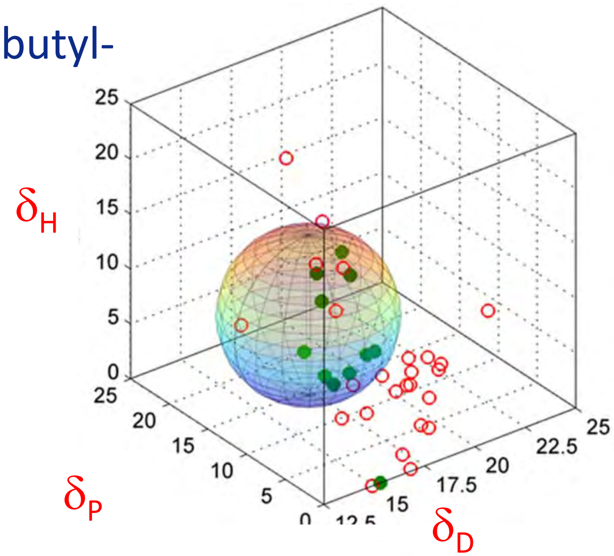
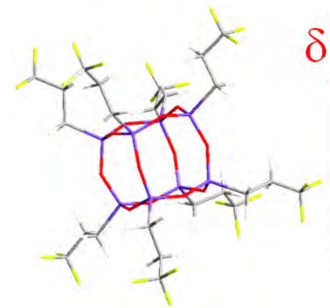
HSP Data for Fluoroalkyl Compounds

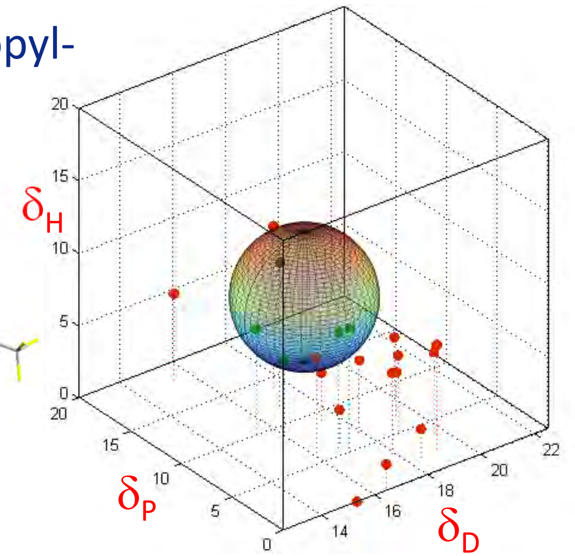
Octa-hexafluoroisobutyl-POSS



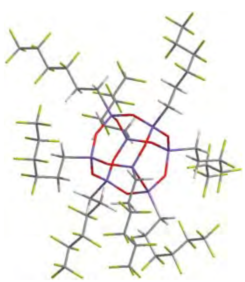


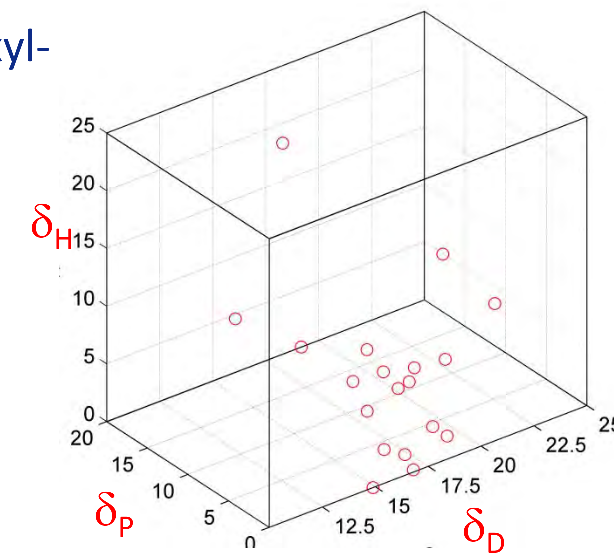
Octa-trifluoropropyl-POSS



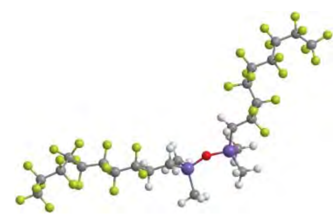


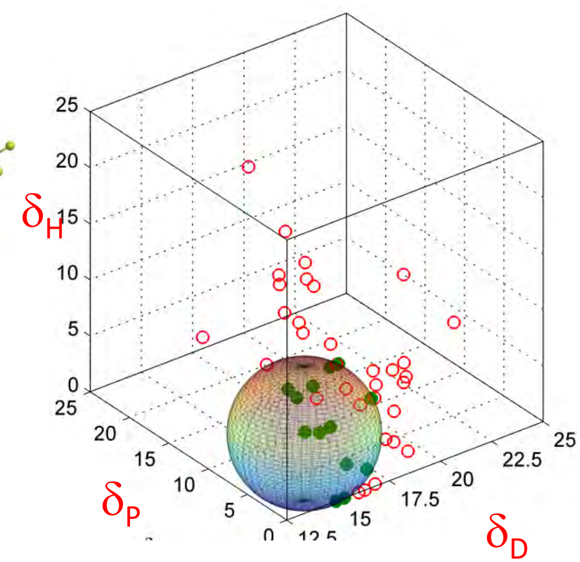
Octa-fluorohexyl-POSS



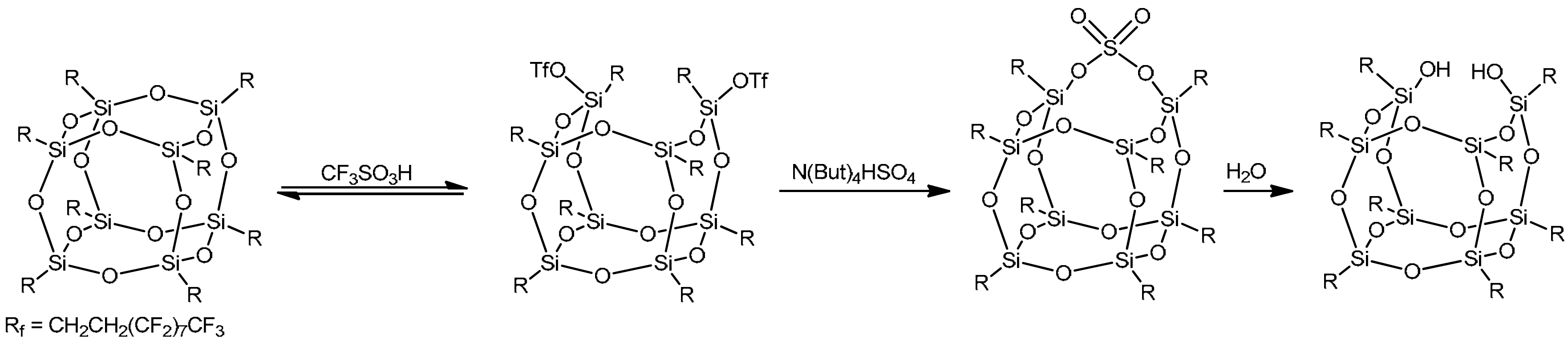


Fluorodecyl-M2

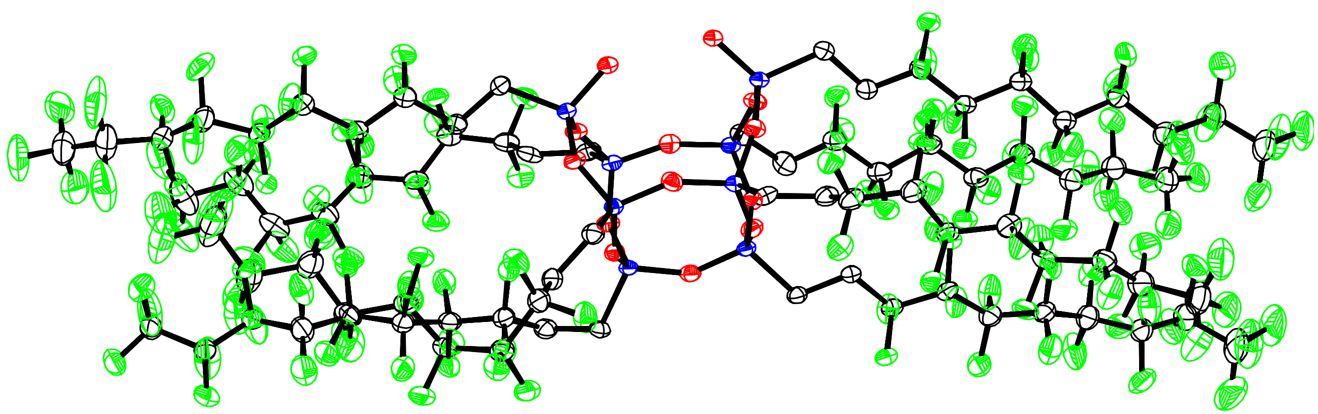




Incompletely Condensed Silsesquioxane



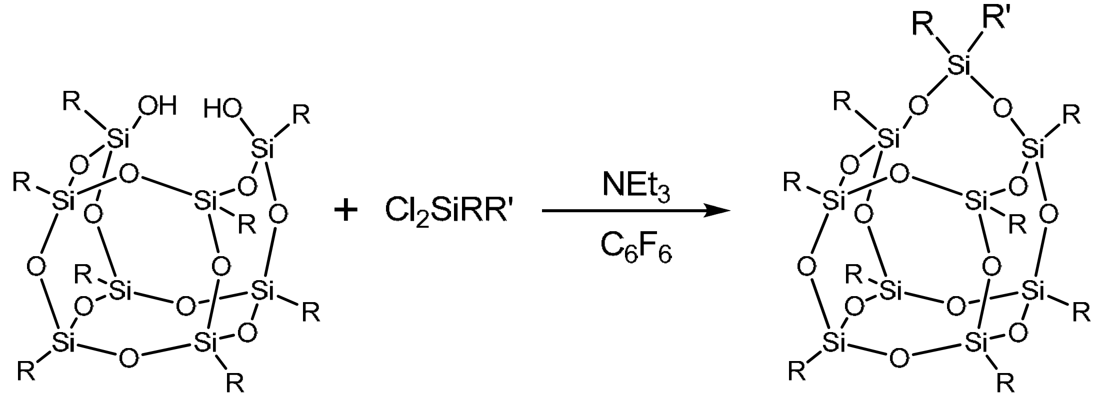
- Incompletely condensed silsesquioxane synthesis yields a disilanol capable of functionalization with dichlorosilanes.



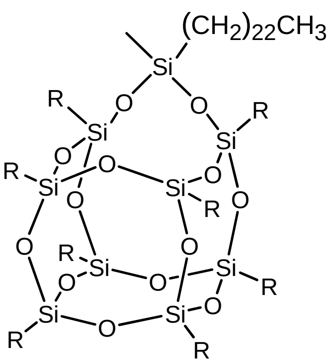
JACS, 2011

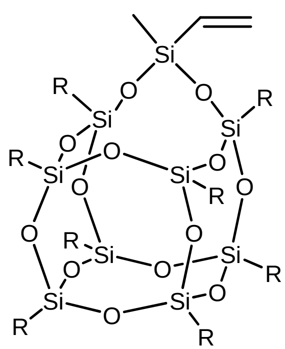
Synthesis of Disilanol FluoroPOSS

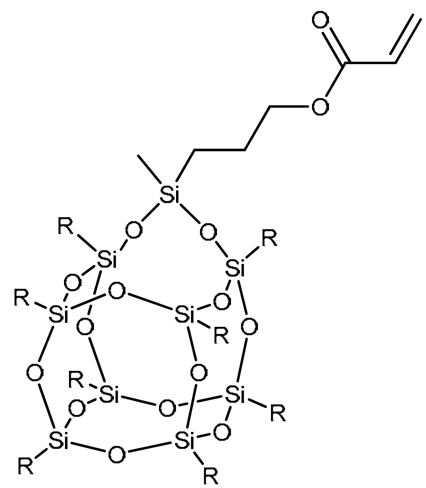
Disilanol FluoroPOSS has a molecular weight of 4009 g/mol.

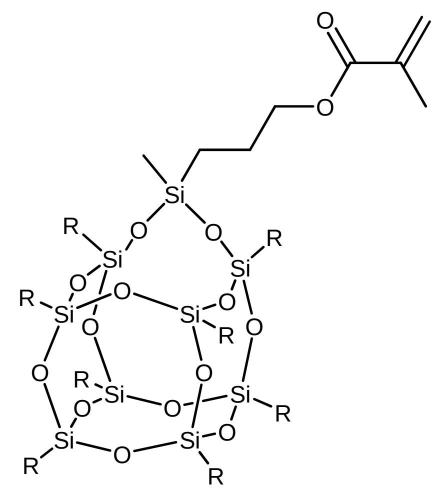


- Can be reacted with functional dichlorosilane to add any desired functionality
- Platform for molecules with superhydrophobic or oleophobic properties
- A variety of fluoroPOSS compounds have been synthesized





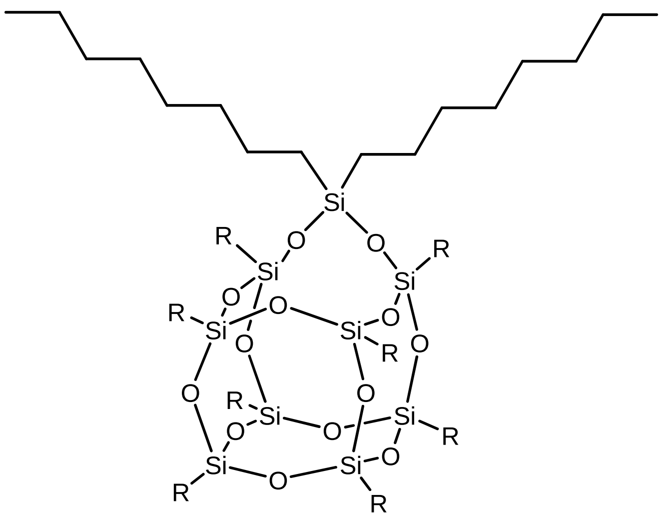


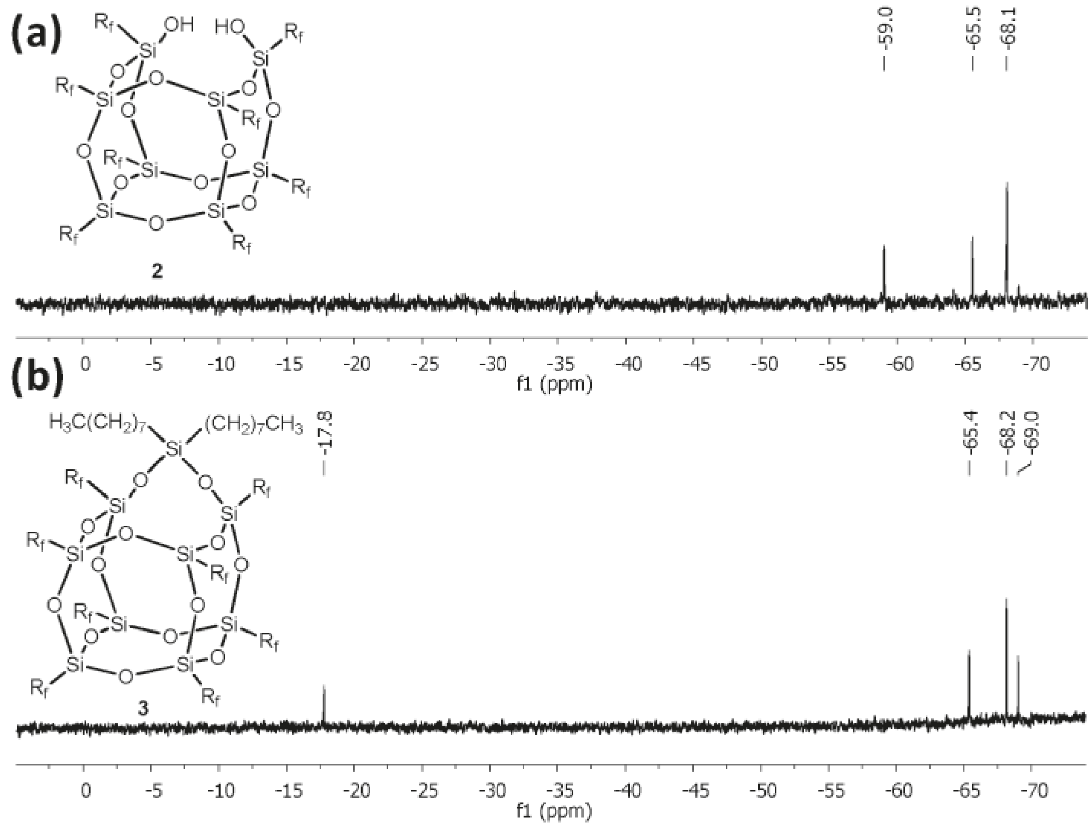


JACS, 2011

Organic-Substituted FluoroPOSS

Dioctyl silyl FluoroPOSS

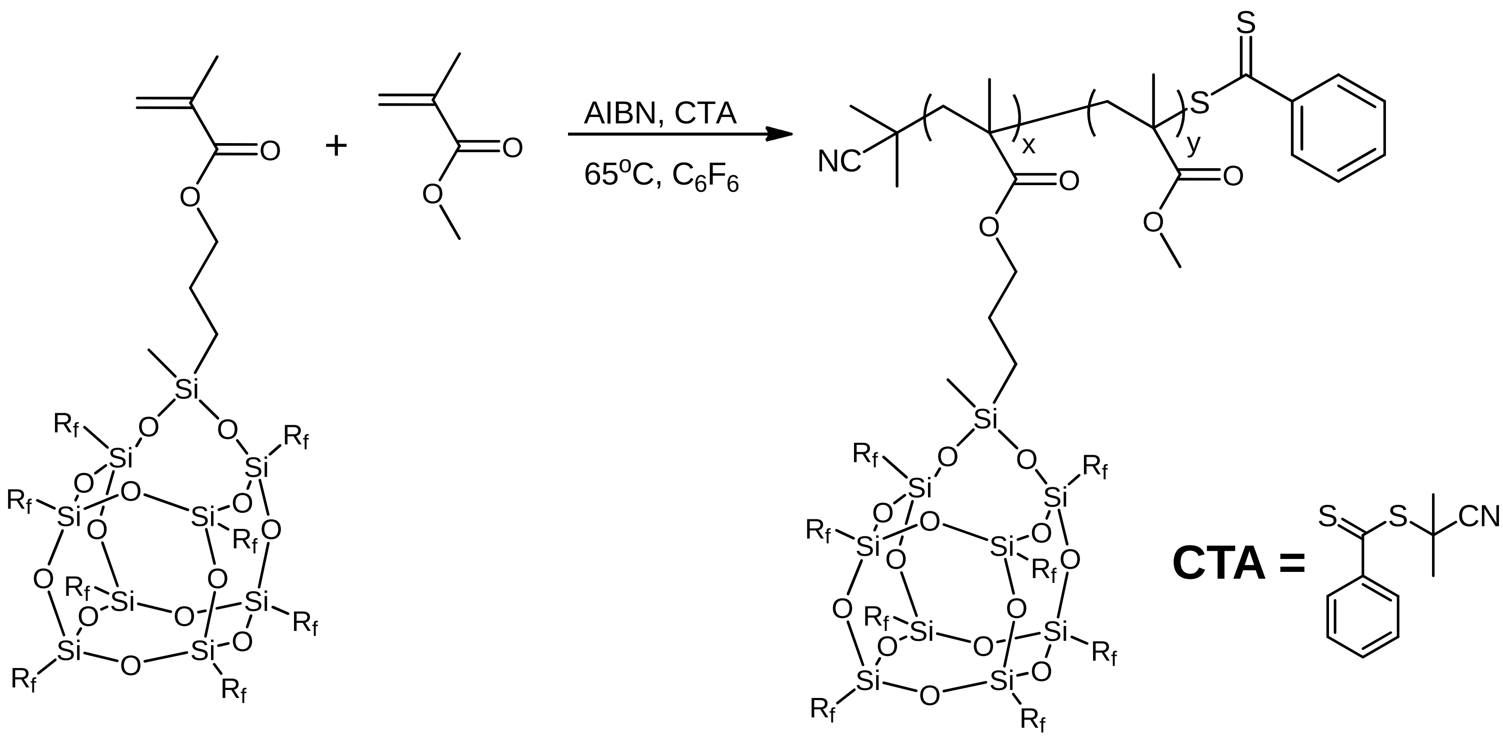




- Soluble in diethyl ether
- Can be directly blended in polymers
- Potential non-ionic surfactants

JACS, 2011

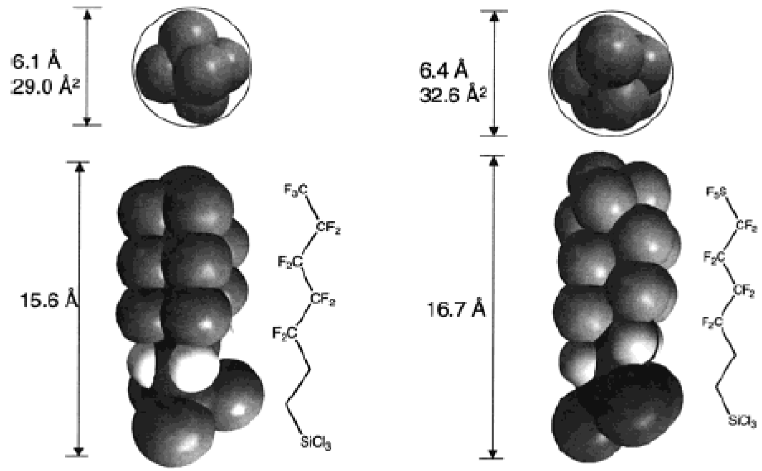
F-POSS Copolymers



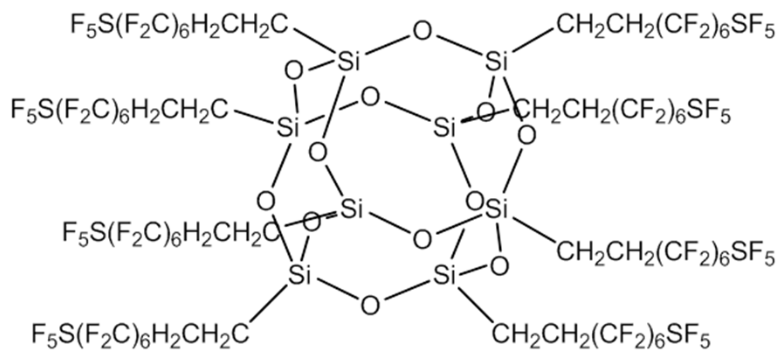
F-POSS wt% (mol%)	M_w (g mol^{-1})	PDI	Conv.%	T_g (°C)	Water (θ_{adv})	Water (θ_{rec})	Hexadecane (θ_{adv})	Hexadecane (θ_{rec})
0	58 100	1.08	73	127	77.8 ± 1.3°	57.8 ± 2.5°	Wetted	Wetted
1 (0.02)	58 700	1.05	72	129	109.2 ± 2.4°	61.5 ± 1.9°	67.8 ± 1.4°	Wetted
5 (0.12)	23 000	1.01	30	124	117.8 ± 1.6°	95.7 ± 2.9°	76.7 ± 1.1°	68.8 ± 1.9°
10 (0.25)	26 900	1.01	29	124	118.2 ± 1.4°	101.1 ± 2.5°	77.2 ± 0.4°	69.5 ± 2.1°
25 (0.79)	37 700	1.03	41	125	120.8 ± 1.8°	97.0 ± 2.4°	82.9 ± 0.4°	74.6 ± 2.0°
F-POSS-MA	n/a	n/a	n/a	n/a	117.1 ± 0.6°	93.8 ± 1.5°	78.1 ± 0.4°	63.0 ± 1.2°

Polym Chem, 2013

SF_5-Terminated F-POSS

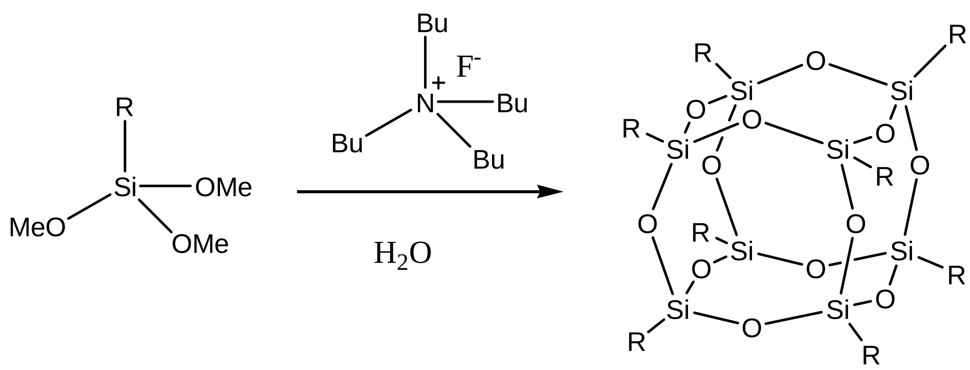


Gard, *Chem Mater*, 2000

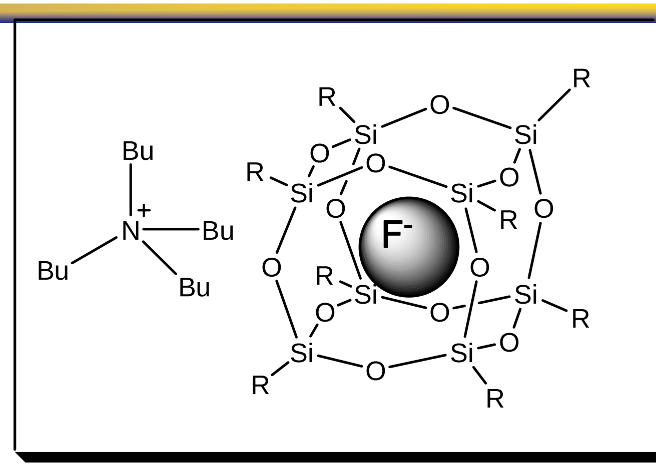


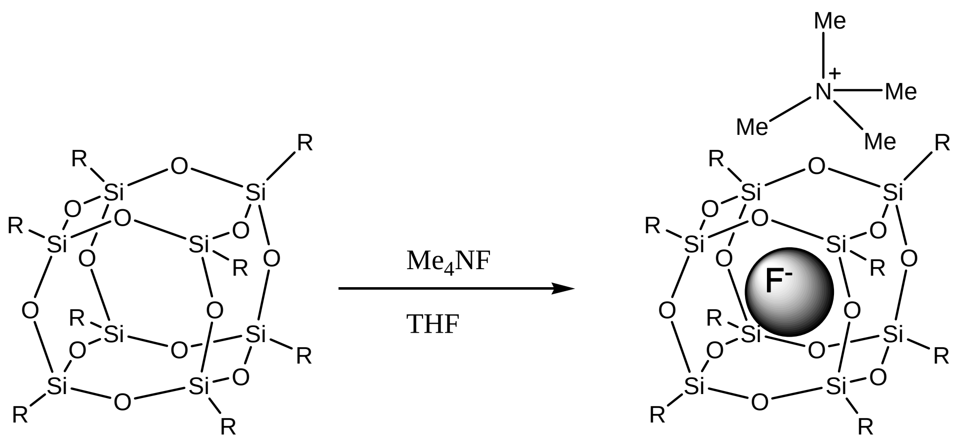
Chemical Formula: $C_{64}H_{32}F_{136}O_{12}S_8Si_8$
Exact Mass: 4055.56

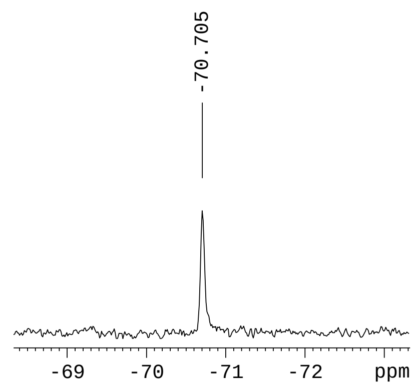
F⁻@F-POSS

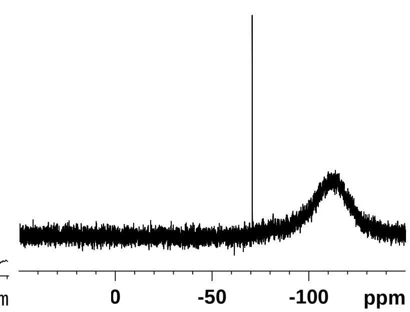


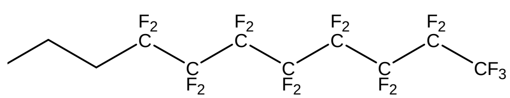
Bassindale, *Angew Chem,* 2003









R = 

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Chem Mater, 2008

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Summary

- Solubility and wetting characteristics vary widely
- Not all types of fluorinated functionality give the same results
- Even minor changes in structure may produce drastically different results
- Solubility behavior is difficult to predict based on structure
- Prediction of water and hydrocarbon wetting behavior is also extremely difficult

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Silicones and Silicone-Modified Materials VII

An International Symposium at the American Chemical Society National Meeting Boston, Massachusetts, August 16-20, 2015

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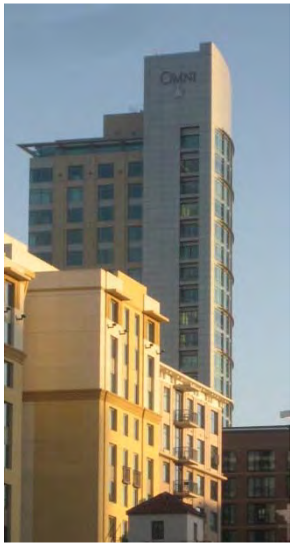
Silicon-Containing Polymers and Composites



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QUESTIONS?
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Comparison of Surface Energy Parameters for POSS Compounds

Table 3. Computed Values of the Dispersion (γ_{sv}^{d}), Acidic (γ_{sv}^{+}), and Basic (γ_{sv}^{-}) Components of Solid-Surface Energy (mN/m) for Various Fluoroalkylated Silicon-Containing Moieties

	alkanes (Zisman analysis)	all liquids[b] (eq 1 with $\varphi_{sl} = 1$)	diiodomethane, dimethyl sulfoxide and water (eq 5)				
	γ_c	γ_{sv}	γ_{sv}	dispersion (γ_{sv}^{d})	polar (γ_{sv}^{p})	acidic (γ_{sv}^{+})	basic (γ_{sv}^{-})
fluorodecyl T_8	5.5	9.3	8.8	8.7	0.1	0.04	0.1
fluorooctyl T_8	7.4	10.6	10.9	10.6	0.3	0.2	0.1
fluorohexyl T_8	8.5	11.6	47.4	11.4	36.0	20.8	15.6
fluoropropyl T_8	19.7	18.7	38.4	19.1	19.3	11.8	7.9
hexafluoro-i-butyl T_8	17.7	19.1	26.9	26.8	0.1	0.002	0.8
fluorodecyl T_8	5.5	9.3	8.8	8.7	0.1	0.04	0.1
fluorodecyl Q_4	14.5	14.3	14.9	14.5	0.8	0.0	0.2
fluorodecyl M_2	19.6	26.8	39.7	30.9	8.8	2.0	9.7

Predicted values based on Hansen Solubiliy Parameters (for "liquid" surfaces)

		γ_{lv} (dyn / cm)	γ^{d}_{lv} (dyn / cm)
Fluorodecyl T8	(est. HSP)	34.6	24.8
Fluorohexyl T8	(est. HSP)	37.7	26.2
Fluoropropyl T8		43.7	28.6
Hexafluoroi-i-butyl T8		43.5	21.4
Fluorodecyl M2		30.3	20.5

- For perfluoroheptane, the predicted value of γ_{lv} of 21 dyn/cm is close to expectations
- Agreement for the dispersive component is better, but γ^{d}_{lv} < γ_{lv} without rearrangement